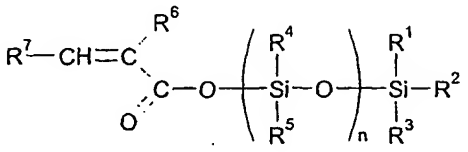
Claims

1. A process for the production of hydrocarbyl silyl unsaturated carboxylates of formula (I).



(I)

wherein

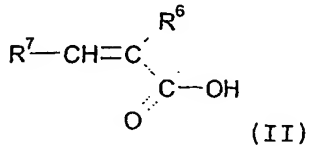
R^1, R^2, R^3, R^4, R^5 each independently represent hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxyl, aryl, aryloxyl, aralkyloxyl, $-O-SiR^1R^2R^3$, $-O-(SiR^4R^5O)_n-SiR^1R^2R^3$ or aralkyl radical optionally substituted by one or more substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxyl, aryl, aryloxyl, silyl, $-O-SiR^1R^2R^3$, $-O-(SiR^4R^5O)_n-SiR^1R^2R^3$, hydroxyl, halogen, amino or amino alkyl radicals, or may independently be an $-O-C(O)-C(R^6)=CHR^7$ group;

R^6 represents a hydrogen atom, or an alkyl group, or $(-R^{11}-)_o\ C(O)OR^{10}$ wherein R^{10} represents an hydrogen atom, $-(SiR^4R^5O)_n-SiR^1R^2R^3$ wherein R^1, R^2, R^3, R^4, R^5 are as already defined or an alkyl group; wherein R^{11} is independently selected from alkyl, alkenyl, alkynyl, aryl or an aralkyl radical optionally substituted by one or more substituents independently selected from alkyl, alkenyl, alkynyl, aralkyl, aryl, hydroxyl, halogen, amino or amino alkyl radicals; O=0 or 1;

R^7 represents a hydrogen atom, or independently represents alkyl, aryl, aralkyl, alkenyl, alkynyl radical optionally substituted with the same radicals as defined for R^6 above or R^7 represents $-COOR^9$ wherein R^9 represents an hydrogen

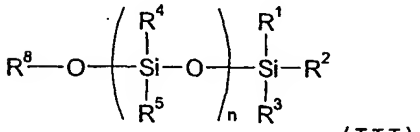
atom, an alkyl group or $-(SiR^4R^5-O)_n-SiR^1R^2R^3$ wherein R^1, R^2, R^3, R^4 and R^5 are as already defined;

by reaction of an unsaturated carboxylic acid of formula (II)



(II)

wherein R^6 and R^7 in formula (II) are as defined above; with a hydrocarbyl silyl compound of formula (III)



(III)

wherein R^1,R^2 ,R^3, R^4 and R^5 are as defined above and R^8 is an hydrogen atom, an alkyl, aralkyl or aryl, alkenyl or alkynyl group optionally substituted with one or more substituents selected from the equivalent substituents as detailed for R^1-R^5 above; and each n above independently represents a number of dihydrocarbylsiloxane units from 0 to 1000; the said reaction being carried out in the presence of a silaphilic catalyst.

2. A process according to claim 1, wherein R^1, R^2, R^3, R^4, R^5 each independently represent an alkyl, an aryl group or a hydrogen atom.

3. A process according to claim 1 or 2, wherein R^1, R^2, R^3, R^4, R^5, R^6 and R^9 are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl.

4. A process according to claims 1, 2 or 3 wherein R^4, R^5, R^6, R^7 and R^9 are independently methyl.

5. A process according to claims 1, 2, 3 or 4 wherein R^1, R^2 and R^3 are n-butyl.

6. A process according to any preceding claim, wherein fluoride containing mineral or organic salts which comprise, but are not limited to, sodium fluoride, potassium fluoride, caesium fluoride or tetrabutyl ammonium fluoride (Bu_4NF); or are selected from N-methyl imidazole(NMI), N,N-dimethylamino pyridine(DMAP), hexamethylphosphoric triamide(HMPA), 4,4 dimethyl imidazole, N methyl-2-pyridone(NMP), pyridine N-oxide, triphenylphosphine oxide, 2,4 dimethyl pyridine, N-methyl-4-pyridone, dimethyl formamide(DMF), 3,5 dimethyl pyridine, N,N-dimethylethylene Urea(DMEU), N,N-dimethylpropylene Urea(DMPU), pyridine, imidazole, trimethylamine, dimethyl sulphoxide(DMSO), N-methyl pyrrolidinone(NMP), formamide, N-alkylformamides, N,N-dialkylformamides, acetamide, N-alkylacetamides, N,N-dialkylacetamides, alkylcyanides, N-methyl pyrrolidone, p-dimethylaminobenzaldehyde, 1,2-dimethyl imidazole, LiOH, LiStearate, NaI, MeONa or MeOLi; the term alkyl in the above N-alkyl and N,N-dialkyl . . . . amides and cyanides includes any linear, cyclic, bicyclic, polycyclic, alkyl aliphatic or aromatic group and in the case of N,N-compounds the alkyl may be the same or different, an example is N-formyl Rosinamine.

7. A process according to any preceding claim, wherein the catalysts are homogenous or heterogenous.

8. A process according to any preceding claim wherein the catalyst is able to coordinate reversibly with the silicon atom.

9. A process according to claim 8, wherein the catalyst is capable of forming a penta or hexa coordinated silicon species.

10. A process according to claim 1, wherein R^1, R^2, R^3, R^4, R^5, R^6, R^8, R^9 and R^7 are alkyl radicals independently selected from methyl, ethyl, n-propyl, isopropyl n-butyl, isobutyl, set-butyl, tert-butyl, 2-methylbutyl, pentyl, iso-amyl, hexyl, cyclohexyl, 3-methylpentyl, octyl and the like.

11. A process according to claim 1, wherein the hydrocarbyl silyl esters of formula I are selected from tri-n-butyl 1-(meth)acryloyloxy-silane, tri-n-propyl-1-(meth)acryloyloxy silane, tri-t-butyl-1-(meth)acryloyloxy-silane, tri-isopropyl-1-(meth)acryloyloxy-silane, tri-isobutyl-1-(meth)acryloyloxy-silane, tri-methyl-1-(meth)acryloyloxy-silane, triethyl- 1-(meth)acryloyloxy-silane, tribenzyl- 1-(meth)acryloyloxy-silane, triamyl- 1-(meth)acryloyloxy-silane, triphenyl- 1-(meth)acryloyloxy-silane, nonamethyl-1-(meth)acryloyloxy-tetrasiloxane, nonaethyl-1-(meth)acryloyloxy-tetrasiloxane, nona-t-butyl-1-(meth)acryloyloxy-tetrasiloxane, nonabenzyl-1-(meth)acryloyloxy-tetrasiloxane, nona-isopropyl-1-(meth)acryloyloxy-tetrasiloxane, nona-n-propyl-1-(meth)acryloyloxy-tetrasiloxane, nona-isobutyl-1-(meth)acryloyloxy-tetrasiloxane, nona-amyl-1-(meth)acryloyloxy-tetrasiloxane, nona-n-butyl-1-(meth)acryloyloxy-tetrasiloxane, nona-dodecyl-1-(meth)acryloyloxy-tetrasiloxane, nona-hexyl-1-(meth)acryloyloxy-tetrasiloxane, nona-phenyl-1-(meth)acryloyloxy-tetrasiloxane, nona-octyl-1-(meth)acryloyloxy-tetrasiloxane, undecamethyl-1-(meth)acryloyloxy-pentasiloxane, undecaethyl-1-(meth)acryloyloxy-pentasiloxane, undeca-t-butyl-1-(meth)acryloyloxy-pentasiloxane, undecabenzyl-1-(meth)acryloyloxy-pentasiloxane, undeca-isopropyl-1-

(meth)acryloyloxy-pentasiloxane, undeca-n-propyl-1-
(meth)acryloyloxy-pentasiloxane, undeca-isobutyl-1-
(meth)acryloyloxy-pentasiloxane, undeca-amyl-1-
(meth)acryloyloxy-pentasiloxane, undeca-n-butyl-1-
(meth)acryloyloxy-pentasiloxane, undeca-dodecyl-1-
(meth)acryloyloxy-pentasiloxane, undeca-hexyl-1-
(meth)acryloyloxy-pentasiloxane, undeca-phenyl-1-
(meth)acryloyloxy-pentasiloxane, undeca-octyl-1-
(meth)acryloyloxy-pentasiloxane tridecamethyl-1-
(meth)acryloyloxy-hexasiloxane, tridecaethyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-t-butyl-1-
(meth)acryloyloxy-hexasiloxane, tridecabenzyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-isopropyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-n-propyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-isobutyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-amyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-n-butyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-dodecyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-hexyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-phenyl-1-
(meth)acryloyloxy-hexasiloxane, trideca-octyl-1-
(meth)acryloyloxy-hexasiloxane -(meth)acryloyloxy-hexasiloxane 1,3,3,3-tetramethyl-1-trimethylsilyloxy-1-(meth)acryloyloxy-disiloxane,
1-ethyl,3,3,3-trimethyl-1-trimethylsilyloxy-1-(meth)acryloyloxy-disiloxane,
tris-(trimethylsilyloxy)-1-methacryloyloxy-silane and polymers thereof.

12. A process according to any preceding claim, wherein the catalysts are independably selected from DMF, DMSO, formamide, N-alkylformamides, N,N-dialkylformamides, acetamide, N-alkylacetamides, N,N-dialkylacetamides, N-Methyl pyrrolidone, p-dimethylaminobenzaldehyde, DMAP, N-methyl imidazole, 1,2-dimethyl imidazole, HMPA, DMPU, NaI, MeONa, MeOLi, Bu4NF, Ph3PO, LiOH, LiStearate and pyridine N-oxide.

13. A process according to any preceding claim, wherein the catalysts are present at a level of 0.001-100 mol% (mol/mol silane).

14. A process according to any preceding claim, wherein the reaction includes a polymeric inhibitor.

15. A process according to any preceding claim, wherein the reaction is carried out in a suitable solvent.

16. A process according to claim 15, wherein suitable solvents include non polar inert solvents, aliphatic hydrocarbons, cyclic and non cyclic ethers.

17. A process according to any claims 15 or 16, wherein the solvent is independently selected from pentane, hexane, heptane, toluene, xylene, benzene, mesitylene, ethylbenzene, octane, decane, decahydronaphthlene, diethyl ether, diisopropyl ether, diisobutyl ether or mixtures thereof.

18. A process according to any of claims 15-17, wherein the solvent causes no distillation of any of the reactants but allows reactive distillation.

19. A process according to any of claims 15-18, wherein the solvent forms a low boiling azeotrope with the distilled R^8OH.

20. A process according to any of claims 15-19, wherein the solvents are independently selected from pentane, hexane, heptane, toluene and xylene.

21. A process according to any preceding claim, wherein the reaction is carried out in the range 0°C - 200°C.

22. A process according to any preceding claim, wherein a polymerisation inhibitor is present in the range 0.001-10% wt/wt of the total reaction mix.

23. A process according to any preceding claim, wherein the molar ratio of silane:acid is between 1:100 and 50:1.

24. A process according to any preceding claim, wherein the solvent is at least 10 wt% of the total reaction mix at the start of the reaction.

25. A hydrocarbyl silyl monomer as defined in formula I produced by a process in accordance with any of claims 1-24.

26. A process according to claim 1, wherein the number of (alk)acryloyl groups in formula I is less than 4.

27. A process according to claim 1, wherein the number of (alk)acryloyl groups in formula I is less than 1.

28. A process according to claim 1, wherein when R^{10} represents alkyl or hydrogen in formula II, it represents $-(SiR^4R^5O-)_nSiR^1R^2R^3$ in formula I, wherein n and R^1-R^5 are as defined previously.

29. A process according to claim 1, wherein when R^1, R^2, R^3, R^4 or R^5 are aryloxyl, alkaryloxyl, alkoxyl or hydroxyl in formula III, they may represent or $-O-C(O)-C(R^6)=CHR^7$ in formula I.

30. A process according to claim 1, wherein where R^9 represents an alkyl group or an hydrogen atom in formula (II), it may represent $-(SiR^4R^5O)_n-SiR^1R^2R^3$ in formula (I).

31. A process according to any of claims 1-6 or 8-30 wherein said catalyst may be a metal alkoxide, an organic

tin compound or a boron compound or cyclic 1,3,5-triisopropoxycyclotrialuminoxane and the like.